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(57) Abstract

There is provided the use of a bleaching species to inhibit the transfer of a bleachable food soil from an aqueous wash solution to a substrate in a dishwashing method wherein said bleaching species is selected from diacyl and tetraacyl peroxide bleaching species and mixtures thereof. There is also provided the use of said bleaching species to enhance the removal of bleachable food soils from a plastic substrate in a dishwashing method.

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DIACYL & TETRAACYL PEROXIDES TO INHIBIT TRANSFER OF BLEACHABLE FOOD SOIL IN MACHINE DISHWASHING

Technical Field

The present invention relates to the use of diacyl and tetraacyl peroxide bleaching species for inhibiting the transfer of bleachable food soils in a dishwashing method. A further aspect of the invention relates to the use of said bleaching species to enhance the removal of bleachable food soils from a plastic substrate in a dishwashing method.

Background of the Invention

A well recognized problem arising during modern fabric laundering operations is the tendency of some coloured fabrics to release dye into the laundry wash solution. The dye is then transferred onto other fabrics being washed therewith.

In dishwashing, especially machine dishwashing, methods there exists a related problem, which is however, not widely recognized in the art. Coloured/bleachable food soils, comprising natural dyestuffs, may be removed from soiled articles into the wash solution, and then may be redeposited from the wash solution onto other articles in the wash or onto the interior of the dishwashing machine.

The problem is particularly noticeable when the washload includes articles soiled by foods naturally containing significant levels of coloured dyestuff molecules, including for example tomato sauce and curry.

The Applicant has found that plastic articles in the wash, and areas of the interior of the dishwashing machine which are made of plastic material, are particularly susceptible to the deposition of coloured food soils from the wash liquor. Said soils can interact with the surface of such plastic substrates producing staining which can be very difficult to remove.

A solution to the problem of dye transfer in laundering operations is to bleach the fugitive dyes washed out of dyed fabrics before they have the opportunity to become attached to other articles in the wash.

A number of the Applicant's copending European Patent Applications have disclosed that certain of the solutions proposed to mitigate dye transfer in laundering operations may also be applied to solve the problem of coloured food dyestuff deposition in a machine dishwashing method.

For example, copending European Patent Application 93870066.3 filed April 9, 1993, provides an efficient dye transfer inhibiting composition for use in a machine dishwashing method. The composition comprises an enzymatic system capable of generating hydrogen peroxide in combination with certain metallo catalysts.

The Applicant has now found that diacyl and/or tetraacyl peroxide bleaching species may be used to inhibit the transfer of coloured/bleachable food soils when employed in a dishwashing, especially machine dishwashing, method. The use of a diacyl and/or tetraacyl peroxide bleaching species for this purpose has not been disclosed in any of the aforementioned prior art documents.

The Applicant has also found that diacyl and/or tetraacyl peroxide bleaching species may be used to enhance the removal of bleachable soils from a plastic substrate when employed in a dishwashing, especially machine dishwashing, method.

Whilst the utility of diacyl and/or tetraacyl peroxide bleaching species to enhance bleachable stain removal has been previously recognized in the

art, including for example PCT Application No. WO 93/07086, the specific utility of such bleaching species in the clean up of stained plastic articles has not previously been recognized. As previously noted, the soiling and related staining of plastic is a particular problem in the dishwashing art.

Summary of the Invention

According to the present invention there is provided the use of a bleaching species to inhibit the transfer of a bleachable food soil from an aqueous wash solution to a substrate in a dishwashing method wherein said bleaching species is selected from diacyl and tetraacyl peroxide bleaching species and mixtures thereof.

According to another aspect of the present invention there is provided the use of a bleaching species to enhance the removal of bleachable food soils from a plastic substrate in a dishwashing method employing an aqueous wash solution wherein said bleaching species is selected from diacyl and tetraacyl peroxide bleaching species and mixtures thereof.

Detailed Description of the Invention

Bleachable food soil transfer inhibition

According to the present invention the bleaching species is used in a dishwashing method for the purpose of inhibiting the transfer of bleachable food soils from an aqueous wash solution to a substrate surface.

By bleachable soils it is meant essentially any coloured food soils which may be decolourised by the action of bleach. The present invention is most especially concerned with the prevention of transfer of hydrophobic bleachable food soils, particularly those having carotenoid chromophores, such as beta-carotene, lycopene, zeaxanthin or capsanthin, hereinafter referred to generically as carotenoid soils. Carotenoid soils can be derived from carrots and

tomatoes, and any processed products containing these components as well as certain tropical fruits and saffron.

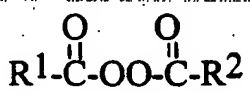
The Applicant has found that the substrate material which is most prone to receipt of the transfer of bleachable food soils is plastic material, such as polypropylene, polyethylene, polystyrene (including alkyl butyl styrene) or PVC. Such plastic substrate material may interact with any bleachable food soils on the substrate surface to produce persistent staining of the substrate. This staining is particularly visible on translucent plastic material, as is commonly employed for food storage boxes and tubs.

According to another aspect of the present invention the bleaching species can also used in a dishwashing method for the purpose of enhancing the removal of bleachable food soils from a previously soiled substrate, wherein the substrate is made from plastic material as hereinabove described.

Diacyl and Tetraacyl Peroxide Bleaching Species

The bleaching species may be selected from essentially any diacyl and tetraacyl peroxide bleaching species and mixtures thereof.

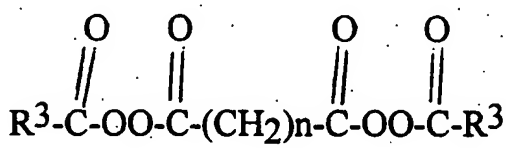
The diacyl peroxide bleaching species is preferably selected from diacyl peroxides of the general formula:



in which R^1 represents an aromatic group or a C_6-C_{18} alkyl, preferably C_6-C_{12} alkyl group containing a linear chain of at least 5 carbon atoms and optionally containing one or more substituents (e.g. $-N^+(CH_3)_3$,-COOH or -CN) and/or one or more interrupting moieties (e.g. -CONH- or -CH=CH-) interpolated between adjacent carbon atoms of the alkyl radical, and R^2 represents an aliphatic or aromatic group compatible with a peroxide moiety, such that R^1 and R^2 together contain a total of 8 to 30 carbon atoms. In one preferred aspect R^1 and R^2 are

linear unsubstituted C_6-C_{12} alkyl chains. In another preferred aspect R^1 and R^2 are phenyl groups. Most preferably R^1 and R^2 are identical. Dibenzoyl peroxide, in which both R^1 and R^2 are phenyl groups, is particularly preferred.

The tetraacyl peroxide bleaching species is preferably selected from tetraacyl peroxides of the general formula:



in which R^3 represents an aromatic group or a C_1-C_9 alkyl, preferably C_3 - C_7, group and n represents an integer from 2 to 12, preferably 4 to 10 inclusive

The diacyl and tetraacyl species are most preferably present as components of a detergent composition. Such species are however intrinsically unstable above their melting points and are liable to self-accelerating thermal decomposition. To provide storage stability it is hence necessary to incorporate the diacyl and tetraacyl bleaching species as "guest" molecules in "host-guest complexes" in which the molecules of the bleaching species are individually separated from each other by their inclusion in the host receptor sites. The hosts may for example be inorganic or organic crystals having relatively open structures which provide sites that may be occupied by guest molecules, thus forming the host-guest complexes. Examples of suitable hosts include certain clathrates or inclusion compounds, including the urea clathrates and the cyclodextrins, particularly the beta-cyclodextrins. The hosts are most preferably water soluble, to enable effective release and dispersion of the bleaching species on introduction of the host-bleaching species complexes into an aqueous media, such as a wash solution. Urea clathrates of diacyl and tetraacyl bleaching species have been disclosed in PCT Application No. WO 93/07086.

The diacyl and tetraacyl bleaching species in themselves have been found to be of particular utility in the bleaching of carotenoid soils, and in the

removal of tea stains. Alternatively, the diacyl and tetraacyl species may act as bleach activator species, and by in situ reaction with perhydroxyl ions form peroxyacids which act to bleach a wide range of soil/stain types. The perhydroxyl ions may originate from, for example, the inorganic perhydrate salts such as the alkali metal perborates and percarbonates.

The diacyl and tetraacyl bleaching species are preferably present in the aqueous wash solution at a total level of from 1 to 100 ppm, more preferably from 5 to 50 ppm most preferably from 10 to 40 ppm by weight of the wash solution.

Dishwashing method

The dishwashing method may be essentially any conventional dishwashing method. Preferably the dishwashing method is a machine dishwashing method performed using a dishwasher machine, which may be selected from any of those commonly available on the market.

The machine dishwashing method typically involves treating soiled tableware, such as crockery, glassware, hollowware and cutlery, with an aqueous wash solution having dissolved or dispersed therein an effective amount of a detergent composition. The diacyl and tetraacyl bleaching species are preferably present as components of said detergent composition.

By an effective amount of detergent composition it is generally meant from 5g to 60g of detergent composition per wash, dissolved or dispersed in an aqueous wash solution volume of from 3 to 10 litres, to provide a wash solution concentration of the detergent composition of from 0.05% to 2% by weight. The wash temperature may be in the range 40°C to 65°C as commonly is employed in such methods. A rinse aid composition may also be used, if desired.

Detergent Compositions

The detergent composition may also contain various other components including surfactants, detergent builders, alkalinity sources, other bleaching agents, lime soap dispersants, organic polymeric compounds including polymeric dye transfer inhibiting agents, crystal growth inhibitors, heavy metal ion sequestrants, enzymes and enzyme stabilizers, corrosion inhibitors, suds suppressors, solvents, and hydrotropes. The diacyl and tetraacyl- bleaching species are preferably present as components of a detergent composition.

Surfactant system

A highly preferred component of the detergent compositions herein is a surfactant system comprising surfactant selected from anionic, cationic, nonionic ampholytic and zwitterionic surfactants and mixtures thereof. The surfactant system is typically present at a level of from 0.5% to 40% by weight, more preferably 1% to 30% by weight, most preferably from 1.5% to 20% by weight of the compositions.

In one preferred execution the surfactant system consists of low foaming nonionic surfactant, preferably selected from ethoxylated and/or propoxylated nonionic surfactants, more preferably selected from nonionic ethoxylated/propoxylated fatty alcohol surfactants.

In an alternative preferred execution the surfactant system comprises high foaming anionic surfactant, particularly alkyl ethoxysulfate surfactant, in combination with a suds suppressing system.

Anionic surfactant

Essentially any anionic surfactants useful for detersive purposes can be included in the compositions. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts

such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary alkyl sulfates, alkyl ethoxysulfates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C_5-C_{17} acyl-N-(C_1-C_4 alkyl) and -N-(C_1-C_2 hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C_6-C_{18} alkyl sulfates which have been ethoxylated with from about 0.5 to about 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C_6-C_{18} alkyl sulfate which has been ethoxylated with from about 0.5 to about 20, preferably from about 0.5 to about 5, moles of ethylene oxide per molecule.

Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C_5-C_{20} linear alkylbenzene sulfonates, alkyl ester sulfonates, C_6-C_{22} primary or secondary alkane sulfonates, C_6-C_{24} olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

Anionic carboxylate surfactants suitable for use herein include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Preferred alkyl ethoxy carboxylates for use herein include those with the formula $RO(CH_2CH_20)_x\ CH_2C00^-M^+$ wherein R is a C_6 to C_{18} alkyl group, x ranges from O to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than about 20 %, and the amount of material where x is greater than 7, is less than about 25 %, the average x is from about 2 to 4 when the average R is C_{13} or less, and the average x is from about 3 to 10 when the average R is greater than C_{13}, and M is a cation, preferably chosen from alkali metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanol-ammonium, most preferably from sodium, potassium, ammonium and mixtures thereof with magnesium ions. The preferred alkyl ethoxy carboxylates are those where R is a C_{12} to C_{18} alkyl group.

Alkyl polyethoxy polycarboxylate surfactants suitable for use herein include those having the formula $RO-(CHR_1-CHR_2-O)-R_3$ wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, wherein at least one R_1 or R_2 is a succinic acid radical or hydroxysuccinic acid radical, and R_3 is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Preferred soap surfactants are secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. The secondary carbon can be in a ring structure, e.g. as in p-octyl benzoic acid, or as in alkyl-substituted cyclohexyl carboxylates. The secondary soap surfactants should preferably contain no ether linkages, no ester linkages and no hydroxyl groups. There should preferably be no nitrogen atoms in the head-group (amphiphilic portion). The secondary soap surfactants usually

contain 11-13 total carbon atoms, although slightly more (e.g., up to 16) can be tolerated, e.g. p-octyl benzoic acid.

The following general structures further illustrate some of the preferred secondary soap surfactants:

A. A highly preferred class of secondary soaps comprises the secondary carboxyl materials of the formula $R^3CH(R^4)COOM$, wherein R^3 is $CH_3(CH_2)x$ and R^4 is $CH_3(CH_2)y$, wherein y can be O or an integer from 1 to 4, x is an integer from 4 to 10 and the sum of (x + y) is 6-10, preferably 7-9, most preferably 8.

B. Another preferred class of secondary soaps comprises those carboxyl compounds wherein the carboxyl substituent is on a ring hydrocarbyl unit, i.e., secondary soaps of the formula R^5-R^6-COOM, wherein R^5 is C^7-C^{10}, preferably C^8-C^9, alkyl or alkenyl and R^6 is a ring structure, such as benzene, cyclopentane and cyclohexane. (Note: R^5 can be in the ortho, meta or para position relative to the carboxyl on the ring.)

C. Still another preferred class of secondary soaps comprises secondary carboxyl compounds of the formula $CH_3(CHR)_k$-$(CH_2)_m$-$(CHR)_n$-$CH(COOM)(CHR)_o$-$(CH2)_p$-$(CHR)_q$-CH_3, wherein each R is C_1-C_4 alkyl, wherein k, n, o, q are integers in the range of 0-8, provided that the total number of carbon atoms (including the carboxylate) is in the range of 10 to 18.

In each of the above formulas A, B and C, the species M can be any suitable, especially water-solubilizing, counterion.

Especially preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid.

Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON (R^1) CH_2 COOM, wherein R is a C_5-C_{17} linear or branched alkyl or alkenyl group, R^1 is a C_1-C_4 alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleyl methyl sarcosinates in the form of their sodium salts.

Nonionic surfactant

Essentially any anionic surfactants useful for detersive purposes can be included in the compositions. Exemplary, non-limiting classes of useful nonionic surfactants are listed below.

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula R^2CONR^1Z wherein : R1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferable C1-C4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R_2 is a C_5-C_{31} hydrocarbyl, preferably straight-chain C_5-C_{19} alkyl or alkenyl, more preferably straight-chain C_9-C_{17} alkyl or alkenyl, most preferably straight-chain C_{11}-C_{17} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl.

Nonionic condensates of alkyl phenols

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use herein. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing

from about 6 to about 18 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide.

Nonionic ethoxylated alcohol surfactant

The alkyl ethoxylate condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from about 2 to about 10 moles of ethylene oxide per mole of alcohol.

Nonionic ethoxylated/propoxylated fatty alcohol surfactant

The ethoxylated C_6-C_{18} fatty alcohols and C_6-C_{18} mixed ethoxylated/propoxylated fatty alcohols are preferred surfactants for use herein, particularly where water soluble. Preferably the ethoxylated fatty alcohols are the C_{10}-C_{18} ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50, most preferably these are the C_{12}-C_{18} ethoxylated fatty alcohols with a degree of ethoxylation from 3 to 40. Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 18 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10.

Nonionic EO/PO condensates with propylene glycol

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by BASF.

Nonionic EO condensation products with propylene oxide/ethylene diamine adducts

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic^{TM} compounds, marketed by BASF.

Nonionic alkylpolysaccharide surfactant

Suitable alkylpolysaccharides for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)t(glycosyl)_x$$

wherein R2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms; n is 2 or 3, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose.

Nonionic fatty acid amide surfactant

Fatty acid amide surfactants suitable for use herein are those having the formula:

$$R^6-\overset{O}{\overset{\|}{C}}-N(R^7)2$$

wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, and $-(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

A suitable example of an alkyl aphodicarboxylic acid for use herein is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Amine Oxide surfactant

Amine oxides useful in the present invention include those compounds having the formula :

$$R^3(OR^4)_xN(R^5)_2 \rightarrow O$$

wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms, preferably 8 to 18 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, preferably 2 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydyroxyalkyl group containing from 1 to 3, preferably from 1 to 2 carbon atoms, or a polyethylene oxide group containing from 1 to 3, preferable 1, ethylene oxide groups. The R^5

groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10}-C_{18} alkyl dimethyl amine oxides and C_8-C_{18} alkoxy ethyl dihydroxyethyl amine oxides. Examples of such materials include dimethyloctylamine oxide, diethyldecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, dimethyldodecylamine oxide, dipropyltetradecylamine oxide, methylethylhexadecylamine oxide, dodecylamidopropyl dimethylamine oxide, cetyl dimethylamine oxide, stearyl dimethylamine oxide, tallow dimethylamine oxide and dimethyl-2-hydroxyoctadecylamine oxide. Preferred are C_{10}-C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide.

Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Betaine surfactant

The betaines useful herein are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C_6-C_{18} hydrocarbyl group, preferably a C_{10}-C_{16} alkyl group or C_{10-16} acylamido alkyl group, each R^1 is typically C_1-C_3 alkyl, preferably methyl,m and R^2 is a C_1-C_5 hydrocarbyl group, preferably a C_1-C_3 alkylene group, more preferably a C_1-C_2 alkylene group. Examples of suitable betaines include coconut acylamidopropyldimethyl betaine; hexadecyl dimethyl betaine; C_{12-14} acylamidopropylbetaine; C_{8-14} acylamidohexyldiethyl betaine; 4[C_{14-16} acylmethylamidodiethylammonio]-1-carboxybutane; C_{16-18} acylamidodimethylbetaine; C_{12-16} acylamidopentanediethyl-betaine; [C_{12-16} acylmethylamidodimethylbetaine. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the C_{10-18} acylamidopropane (or

ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Sultaine surfactant

The sultaines useful herein are those compounds having the formula $(R(R^1)_2N^+R^2SO_3^-$ wherein R is a C_6-C_{18} hydrocarbyl group, preferably a C_{10}-C_{16} alkyl group, more preferably a C_{12}-C_{13} alkyl group, each R^1 is typically C_1-C_3 alkyl, preferably methyl, and R^2 is a C_1-C_6 hydrocarbyl group, preferably a C_1-C_3 alkylene or, preferably, hydroxyalkylene group.

Ampholytic surfactant

Ampholytic surfactants can be incorporated into the detergent compositions herein. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched.

Cationic surfactants

Cationic surfactants can also be used in the detergent compositions herein. Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C_6-C_{16}, preferably C_6-C_{10} N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Detergent Builder System

A highly preferred component of the detergent compositions herein is a detergent builder system wherein said detergent builder system is preferably present at a level of from 0.5% to 80% by weight, more preferably from 1% to 60% by weight, most preferably from 2% to 40% weight of the compositions.

The detergent builder system is preferably water-soluble, and can, for example, contain builder compound selected from monomeric polycarboxylates or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more that two carbon atoms, the alkali metal, ammonium or alkanonammonium salts of bicarbonates, borates, phosphates, and mixtures of any of the foregoing.

Suitable water-soluble monomeric or oligomeric carboxylate builders can be selected from a wide range of compounds but such compounds preferably have a first carboxyl logarithmic acidity/constant (pK_1) of less than 9, preferably of between 2 and 8.5, more preferably of between 4 and 7.5.

The carboxylate or polycarboxylate builder can be momomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance. Monomeric and oligomeric builders can be selected from acyclic, alicyclic, heterocyclic and aromatic carboxylates.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the

oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as components of builder systems of the detergent compositions.

Specific examples of carbonate builder compound include the alkali metal carbonates, bicarbonates and sesquicarbonates.

Specific examples of phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium

pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid. Preferably, no phosphate builder compound is present.

The compositions may also include less water soluble builders although preferably their levels of incorporation are minimized. Examples of such less water soluble builders include the crystalline layered silicates, and the largely water insoluble sodium aluminosilicates.

Alkalinity

An alkalinity source is a preferred component of the compositions herein. A useful alkalinity source is provided by silicates which also provide china care properties to the detergent formulation. Suitable silicates include the water soluble sodium silicates with an SiO_2: Na_2O ratio of from 1.0 to 2.8, with ratios of from 1.6 to 2.4 being preferred, and 2.0 ratio being most preferred. The silicates may be in the form of either the anhydrous salt or a hydrated salt. Sodium silicate with an SiO_2: Na_2O ratio of 2.0 is the most preferred silicate.

Silicates are preferably incorporated in the compositions of the invention at a level of from 1% to 50%, preferably from 5% to 40%, most preferably from 5% to 30% by weight.

Additional bleaching agents

The detergent compositions herein may include bleaching agents, additional to any diacyl or tetraacyl peroxide bleaching species, selected from chlorine bleaches, inorganic perhydrate salts, peroxyacid bleach precursors and organic peryoxacids.

There may be provided a means of delaying the release of oxygen bleach, which could include any diacyl and/or tetraacyl bleaching species, into the wash solution. Said means may be provided, for example by coating a granular bleach component with a hydrophobic coating, or by choice of

physical form of the bleach which has a slow rate of dissolution by virtue, for example of its density or particle size.

Delayed release of the oxyegn bleach into the wash solution can be advantageous in the prevention of tarnishing of silverware in washload, particularly when a component designed to protectively coat the silver in the wash is also included in the formulation. Such silver tarnish prevention technologies are disclosed in the Applicant's co-pending European Applications Nos. 9370004.4, 93870090.3, 93201918.5 and 93202095.1.

Chlorine bleaching agents

Chlorine bleaches include the alkali metal hypochlorites and chlorinated cyanuric acid salts. The use of chlorine bleaches in the composition of the invention is preferably minimized, and more preferably the compositions contain no chlorine bleach.

Inorganic perhydrate bleaching agents

The detergent compositions herein preferably include an inorganic perhydrate salt, normally in the form of the sodium salt preferably at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however, the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product.

Sodium perborate can be in the form of the monohydrate of nominal formula $NaBO_2H_2O_2$ or the tetrahydrate $NaBO_2H_2O_2.3H_2O$.

Sodium percarbonate, which is a preferred perhydrate for inclusion in detergent compositions in accordance with the invention, is an addition compound having a formula corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid. The percarbonate is most preferably incorporated into such compositions in coated form. The most preferred coating material comprises mixed salt of an alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $Na_2SO_4.n.Na_2CO_3$ wherein n is form 0.1 to 3, preferably n is from 0.15 to 1.0 and most preferably n is from 0.2 to 0.5.

Another suitable coating material is sodium silicate of SiO_2 : Na_2O ratio from 1.6 : 1 to 3.4 : 1, preferably 2.8 : 1, applied as an aqueous solution to give a level of from 2% to 10%, (normally from 3% to 5%) of silicate solids by weight of the percarbonate. Magnesium silicate can also be included in the coating. Other suitable coating materials include the alkali and alkaline earth metal sulphates and carbonates.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of usefulness in the detergent compositions.

Peroxyacid bleach precursors

The detergent compositions herein also preferably include a peroxyacid bleach precursor (bleach activator), usually in combination with an inorganic perhydrate salt. Peroxyacid bleach precursors are normally incorporated at a level of from 1% to 20% by weight, more preferably from 1% to 10% by weight, most preferably from 1% to 7% by weight of the compositions.

The peroxyacid bleach precursors typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides and acylated

derivatives of imidazoles and oximes, and examples of useful materials within these classes are disclosed in GB-A-1586789. The most preferred classes are esters such as are disclosed in GB-A-836988, 864798, 1147871 and 2143231 and imides such as are disclosed in GB-A-855735 & 1246338.

Particularly preferred bleach precursor compounds are the N,N,N^1,N^1 tetra acetylated compounds of formula $(CH_3CO)_2$-$(CH_2)_x$-$(CH_3CO)_2$ wherein x can be O or an integer between 1 & 6.

Examples include tetra acetyl methylene diamine (TAMD) in which x=1, tetra acetyl ethylene diamine (TAED) in which x=2 and tetraacetyl hexylene diamine (TAHD) in which x=6. These and analogous compounds are described in GB-A-907356. The most preferred peroxyacid bleach precursor is TAED.

Another preferred class of peroxyacid bleach activator compounds are the amide substituted compounds described in EP-A-0170386.

Other peroxyacid bleach precursor compounds include sodium trimethyl hexanoyloxy benzene sulfonate and sodium acetoxy benzene sulfonate.

Organic peroxyacids

The detergent compositions may also contain organic peroxyacids at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition.

Useful organic peroxyacids include the amide substituted peroxyacids described in EP-A-0170386.

Other organic peroxyacids include diperoxy dodecanedioc acid, diperoxy tetra decanedioc acid, diperoxyhexadecanedioc acid, mono- and diperazelaic acid, mono- and diperbrassylic acid, monoperoxy phthalic acid, perbenzoic acid, and their salts as disclosed in, for example, EP-A-0341 947.

Lime soap dispersant compound

The compositions herein may contain a lime soap dispersant compound, which has a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6. The lime soap dispersant compound is preferably present at a level of from 0.1% to 40% by weight, more preferably 1% to 20% by weight, most preferably from 2% to 10% by weight of the compositions.

A lime soap dispersant is a material that prevents the precipitation of alkali metal, ammonium or amine salts of fatty acids by calcium or magnesium ions. A numerical measure of the effectiveness of a lime soap dispersant is given by the lime soap dispersing power (LSDP) which is determined using the lime soap dispersion test as described in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to , for example, in the following review articles; W.N. Linfield, Surfactant Science Series, Volume 7, p3; W.N. Linfield, Tenside Surf. Det. , Volume 27, pages159-161, (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, Volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm $CaCO_3$ (Ca:Mg=3:2) equivalent hardness.

Polymeric lime soap dispersants suitable for use herein are described in the article by M.K. Nagarajan and W.F. Masler, to be found in Cosmetics and Toiletries, Volume 104, pages 71-73, (1989). Examples of such polymeric lime soap dispersants include certain water-soluble salts of copolymers of acrylic acid, methacrylic acid or mixtures thereof, and an acrylamide or substituted acrylamide, where such polymers typically have a molecular weight of from 5,000 to 20,000.

Surfactants having good lime soap dispersant capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

Exemplary surfactants having a LSDP of no more than 8 for use in accord with the invention include C_{16}-C_{18} dimethyl amine oxide, C_{12}-C_{18} alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly C_{12}-C_{15} alkyl ethoxysulfate surfactant with a degree of ethoxylation of about 3 (LSDP=4), and the C_{13}-C_{15} ethoxylated alcohols with an average degree of ethoxylation of either 12 (LSDP=6) or 30, sold under the trade names Lutensol A012 and Lutensol A030 respectively, by BASF GmbH.

Organic polymeric compound

Organic polymeric compounds may be added to the detergent compositions herein. By organic polymeric compounds it is meant essentially any polymeric organic compounds commonly used as dispersants, anti-redeposition and soil suspension agents in detergent compositions.

Organic polymeric compound may be incorporated into the detergent compositions of the invention at a level of from 0.05% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Organic polymers containing acrylic acid or its salts having an average molecular weight of less than 15,000, hereinafter referred to as low molecular weight acrylic acid containing polymer, are particularly preferred organic polymeric compounds herein.

The low molecular weight acrylic acid containing polymers preferably have an average molecular weight of less than 15,000, preferably from 500 to 12,000, more preferably from 1,500 to 10,000, most preferably from 2,500 to 9,000.

The low molecular weight acrylic acid containing polymers may be either homopolymers or copolymers including the essential acrylic acid or acrylic acid salt monomer units. Copolymers may include essentially any suitable other monomer units including modified

acrylic, fumaric, maleic, itaconic, aconitic, mesaconic, citraconic and methylenemalonic acid or their salts, maleic anhydride, acrylamide, alkylene, vinylmethyl ether, styrene and any mixtures thereof.

Preferred commercially available low molecular weight acrylic acid containing homopolymers include those sold under the tradename Sokalan PA30, PA20, PA15 and PA10 by BASF GmbH, and those sold under the tradename Acusol 45N by Rohm and Haas.

Preferred low molecular weight acrylic acid containing copolymers include those which contain as monomer units: a) from 90% to 10%, preferably from 80% to 20% by weight acrylic acid or its salts and b) from 10% to 90%, preferably from 20% to 80% by weight of a substituted acrylic monomer or its salts having the general formula -[CR_2-CR_1(CO-O-R_3)]- wherein at least one of the substituents R_1, R_2 or R_3, preferably R_1 or R_2 is a 1 to 4 carbon alkyl or hydroxyalkyl group, R_1 or R_2 can be a hydrogen and R_3 can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R_1 is methyl, R_2 is hydrogen (i.e. a methyl acrylic acid monomer). The most preferred copolymer of this type has a molecular weight of 3500 and contains 60% to 80% by weight of acrylic acid and 40% to 20% by weight of methyl acrylic acid.

Preferred commercially available low molecular weight acrylic acid containing copolymers include those sold under the tradename Sokalan CP10 by BASF GmbH.

Other suitable polyacrylate/modified polyacrylate copolymers include those copolymers of unsaturated aliphatic carboxylic acids disclosed in U.S. Patents No.s 4,530,766, and 5,084,535 which have a molecular weight of less than 15,000.

Further examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are the copolymers of

polyacrylate with maleic anhydride having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Other suitable organic polymeric compounds include the polymers of acrylamide and acrylate having a molecular weight of from 16,000 to 100,000, and the acrylate/fumarate copolymers having a molecular weight of from 16,000 to 80,000.

The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose.

Further useful organic polymeric compounds are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000.

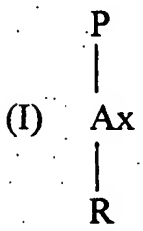
Polymeric dye transfer inhibiting agents

The detergent compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof.

a) Polyamine N-oxide polymers

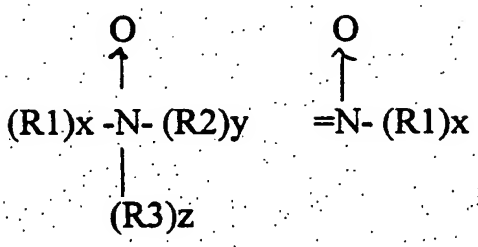
Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :



wherein P is a polymerisable unit, whereto the R-N-O group can be attached to, or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the

nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic,heterocyclic or alicyclic groups wherein the nitrogen of the N-0 functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-0 functional group is attached to said R groups. Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes,

polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a PKa < 10, preferably PKa < 7, more preferred PKa < 6.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

Preferred polymers for use herein may comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 2O,000. The preferred N-vinylimidazole N-vinylpyrrolidone copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4 .

c) Polyvinylpyrrolidone

The detergent compositions herein may also utilize polyvinylpyrrolidone ("PVP" having an average molecular

weight of from 2,500 to 400,000, preferably from 5,000 to 200,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000. Suitable polyvinylpyrrolidones are commercially vailable from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

Polyvinylpyrrolidone may be incorporated in the detergent compositions herein at a level of from 0.01% to 5% by weight of the detergent, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight. The amount of polyvinylpyrrolidone delivered in the wash solution is preferably from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

d) Polyvinyloxazolidone

The detergent compositions herein may also utilize polyvinyloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinyloxazolidones have an average molecular weight of from 2,500 to 400,000, preferably from 5,000 to 200,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000.

The amount of polyvinyloxazolidone incorporated in the detergent compositions may be from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight. The amount of polyvinyloxazolidone delivered in the wash solution is typically from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

e) Polyvinylimidazole

The detergent compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000, more preferably from 5,000 to 50,000, and most preferably from 5,000 to 15,000.

The amount of polyvinylimidazole incorpoarted in the detergent compositions may be from 0.01% to 5% by weight, preferably from 0.05% to 3% by weight, and more preferably from 0.1% to 2% by weight. The amount of polyvinylimidazole delivered in the wash solution is from 0.5 ppm to 250 ppm, preferably from 2.5 ppm to 150 ppm, more preferably from 5 ppm to 100 ppm.

Heavy metal ion sequestrants

Heavy metal ion sequestrants are useful components herein. By heavy metal ion sequestrants it is meant components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they bind heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are preferably present at a level of from 0.005% to 20%, more preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the compositions.

Heavy metal ion sequestrants, which are acidic in nature, having for example phosphonic acid or carboxylic acid functionalities, may be present either in their acid form or as a complex/salt with a suitable counter cation such as an alkali or alkaline metal ion, ammonium, or substituted ammonium ion, or any mixtures thereof. Preferably any salts/complexes are water soluble. The molar ratio of said counter cation to the heavy metal ion sequestrant is preferably at least 1:1.

Suitable heavy metal ion sequestrants for use herein include the organo aminophosphonates, such as the amino alkylene poly (alkylene phosphonates) and nitrilo trimethylene phosphonates. Preferred organo aminophosphonates are diethylene triamine penta (methylene phosphonate) and hexamethylene diamine tetra (methylene phosphonate).

Other suitable heavy metal ion sequestrants for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminotetracetic acid, ethylenetriamine pentacetic acid, or ethylenediamine disuccinic acid. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS), most preferably present in the form of its S,S isomer, which is preferred for its biodegradability profile.

Still other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EPA 317 542 and EPA 399 133.

In one preferred aspect of the invention any heavy metal ion sequestrant, particularly where said sequestrant comprises organo aminophosphonate components, is sprayed onto powdered sodium sulphate prior to incorporation into granular compostions in accord with the invention. This step leads to enhanced sequestrant stability in the granular detergent matrix.

Crystal growth inhibitor

A preferred component of the detergent compositions herein is a crystal growth inhibitor selected from organo diphosphonic acid or one of its salts/complexes. The organo diphosphonic acid component is preferably present at a level of from 0.005% to 20%, more preferably from 0.1% to 10%, most preferably from 0.2% to 5% by weight of the compositions.

The organo diphosphonic acid component may be present in its acid form or in the form of one of its salts or complexes with a suitable counter cation and reference hereinafter to the acid implicitly includes reference to said salts or complexes. Preferably any salts/complexes are water soluble, with the alkali metal and alkaline earth metal salts/complexes being especially preferred.

The organo diphosphonic acid is preferably a C_1-C_4 diphosphonic acid, more preferably a C_2 diphosphonic acid, such as ethylene diphosphonic acid, or most preferably ethane 1-hydroxy-1,1-diphosphonic acid (HEDP).

Enzyme

Another optional ingredient useful in the detergent compositions herein is one or more enzymes.

Preferred enzymatic materials include the commercially available lipases, amylases, neutral and alkaline proteases, esterases, cellulases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are discussed in US Patents 3,519,570 and 3,533,139.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold under the tradename FN, FNA and FN-2 by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Preferred amylases include, for example, -amylases obtained from a special strain of B licheniforms, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S.

Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme (lipase) may be present at levels of active lipolytic enzyme of from 0.0001% to 2% by weight, preferably 0.001% to 1% by weight, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp.or Thermomyces sp. or Pseudomonas pseudoalcaligenes or Pseudomas fluorescens. Lipase from chemically or genetically modified mutants of these strains are also useful herein.

A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

Enzyme Stabilizing System

Enzyme-containing compositions herein may comprise from 0.001% to 10%, preferably from 0.005% to 8%,most preferably from 0.01% to 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detersive enzyme. Such stabilizing systems can comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acid, boronic acid, and mixtures thereof. Such stabilizing systems can also comprise reversible protease inhibitors.

The compositions herein may further comprise from 0% to 10%, preferably from 0.01% to 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from 0.5 ppm to 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme during washing is usually large; accordingly, enzyme stability in-use can be problematic.

Suitable chlorine scavenger anions are widely available, and are illustrated by salts containing ammonium cations or sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc. and mixtures thereof can be used if desired.

Corrosion inhibitor

The compositions may also contain corrosion inhibitor which is preferably incorporated at a level of from 0.05% to 10%, preferably from 0.1% to 5% by weight of the composition.

Suitable corrosion inhibitors include paraffin oil typically a predominantly branched aliphatic hydrocarbon having a number of carbon atoms in the range of from 20 to 50; preferred paraffin oil selected from predominantly branched C_{25-45} species with a ratio of cyclic to noncyclic hydrocarbons of about 32:68; a paraffin oil meeting these characteristics is sold by Wintershall, Salzbergen, Germany, under the trade name WINOG 70.

Other suitable corrosion inhibitor compounds include benzotriazole and any derivatives thereof, mercaptans and diols, especially mercaptans with 4 to 20 carbon atoms including lauryl mercaptan, thiophenol, thionapthol,

thionalide and thioanthranol. Also suitable are the C_{12}-C_{20} fatty acids, or their salts, especially aluminium tristearate. The C_{12}-C_{20} hydroxy fatty acids, or their salts, are also suitable. Phosphonated octa-decane and other anti-oxidants such as betahydroxytoluene (BHT) are also suitable.

Suds suppressing system

The compositions herein may comprise a suds suppressing system preferably present at a level of from 0.01% to 15%, more preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition. A suds suppressing system is a highly preferred component of the compositions when the surfactant system comprises high foaming surfactant.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds, 2-alkyl alcanol antifoam compounds, and paraffin antifoam compounds.

By antifoam compound it is meant herein any compound or mixtures of compounds which act such as to depress the foaming or sudsing produced by a solution of a detergent composition, particularly in the presence of agitation of that solution.

Particularly preferred antifoam compounds for use herein are silicone antifoam compounds defined herein as any antifoam compound including a silicone component. Such silicone antifoam compounds also typically contain a silica component. The term "silicone" as used herein, and in general throughout the industry, encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl group of various types.

Other suitable antifoam compounds include the monocarboxylic fatty acids and soluble salts thereof. These materials are described in US Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids, and salts thereof, for use as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms,

preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

Other suitable antifoam compounds include, for example, high molecular weight hydrocarbons such as paraffin, fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C_{18}-C_{40} ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters. The hydrocarbons, such as paraffin and haloparaffin, can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 5°C, and a minimum boiling point not less than 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms.

Copolymers of ethylene oxide and propylene oxide, particularly the mixed ethoxylated/propoxylated fatty alcohols with an alkyl chain length of from 10 to 16 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10, are also suitable antifoam compounds for use herein.

Suitable 2-alky-alcanols antifoam compounds for use herein have been described in DE 40 21 265. The 2-alkyl-alcanols suitable for use herein consist of a C_6 to C_{16} alkyl chain carrying a terminal hydroxy group, and said alkyl chain is substituted in the alpha position by a C_1 to C_{10} alkyl chain. Mixtures of 2-alkyl-alcanols can be used in the compositions according to the present invention.

Solvent

The compositions herein may contain organic solvents, particularly when formulated as liquids or gels. The compositions in accord with the invention preferably contain a solvent system present at levels of from 1% to 30% by weight, preferably from 3% to 25% by weight, more preferably form 5% to 20% by weight of the composition. The solvent system may be a mono, or mixed solvent system. Preferably, at least the major component of the solvent system is of low volatility.

Suitable organic solvent for use herein has the general formula $RO(CH_2C(Me)HO)_nH$, wherein R is an alkyl, alkenyl, or alkyl aryl group having from 1 to 8 carbon atoms, and n is an integer from 1 to 4. Preferably, R is an alkyl group containing 1 to 4 carbon atoms, and n is 1 or 2. Especially preferred R groups are n-butyl or isobutyl. Preferred solvents of this type are 1-n-butoxypropane-2-ol (n=1); and 1(2-n-butoxy-1-methylethoxy)propane-2-ol (n=2), and mixtures thereof.

Other solvents useful herein include the water soluble CARBITOL solvents or water-soluble CELLOSOLVE solvents. Water-soluble CARBITOL solvents are compounds of the 2-(2-alkoxyethoxy)ethanol class wherein the alkoxy group is derived from ethyl, propyl or butyl; a preferred water-soluble carbitol is 2-(2-butoxyethoxy)ethanol also known as butyl carbitol. Water-soluble CELLOSOLVE solvents are compounds of the 2-alkoxyethoxy ethanol class, with 2-butoxyethoxyethanol being preferred.

Other suitable solvents are benzyl alcohol, and diols such as 2-ethyl-1,3-hexanediol and 2,2,4-trimethl-1,3-pentanediol.

The low molecular weight, water-soluble, liquid polyethylene glycols are also suitable solvents for use herein.

The alkane mono and diols, especially the C_1-C_6 alkane mono and diols are suitable for use herein. C_1-C_4 monohydric alcohols (eg: ethanol, propanol, isopropanol, butanol and mixtures thereof) are preferred, with

ethanol particularly preferred. The C1-C4 dihydric alcohols, including propylene glycol, are also preferred.

Hydrotropes

Hydrotrope may be added to the compositions herein, and is typically present at levels of from 0.5% to 20%, preferably from 1% to 10%, by weight.

Useful hydrotropes include sodium, potassium, and ammonium xylene sulfonates, sodium, potassium, and ammonium toluene sulfonate, sodium potassium and ammonium cumene sulfonate, and mixtures thereof.

Other optional ingredients

Other optional ingredients suitable for inclusion in the compositions herein include perfumes, colours and fillers.

pH of the compositions

The compositions preferably have a pH as a 1% solution in distilled water at 20°C of from 8.5 to 13.0, preferably from 9.5 to 11.5, most preferably from 9.8 to 11.0.

The pH of the compositions may be adjusted by the use of various pH adjusting agents. Preferred acidification agents include inorganic and organic acids including, for example, carboxylate acids, such as citric and succinic acids. Bicarbonates, particularly sodium bicarbonate, are useful pH adjusting agents herein. A highly preferred acidification acid is citric acid which has the advantage of providing builder capacity to the wash solution.

Form of the compositions

The detergent compositions herein can be formulated in any desirable form such as powders, tablets, granulates, pastes, liquids and gels.

Liquid compositions

The detergent compositions herein may be formulated as liquid compositions which typically comprise from 94% to 35% by weight, preferably from 90% to 40% by weight, most preferably from 80% to 50% by weight of a liquid carrier, e.g., water, preferably a mixture of water and organic solvent.

Gel compositions

Gel compositions are typically formulated with polyakenyl polyether having a molecular weight of from about 750,000 to about 4,000,000.

Solid compositions

The detergent compositions herein may also be in the form of solids, such as powders, granules and tablets.

The particle size of the components of granular compositions should preferably be such that no more that 5% of particles are greater than 1.4mm in diameter and not more than 5% of particles are less than 0.15mm in diameter.

The bulk density of granular detergent compositions is typically at least 450 g/litre, more usually at least 600 g/litre and more preferably from 650 g/litre to 1000 g/litre.

Making processes - granular compositions

In general, granular detergent compositions can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation.

EXAMPLES

The following examples illustrate the present invention.

In the following compositions, the abbreviated identifications have the following meanings:

Citrate :	Trisodium citrate dihydrate
Nonionic:	C_{13}-C_{15} mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5 sold under the tradename Plurafac LF404 by BASF Gmbh.
HEDP :	Ethane 1-hydroxy-1,1-diphosphonic acid
DETPMP :	Diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto under the tradename Dequest 2060
MA/AA:	Copolymers of 1:4 maleic/acrylic acid, average molecular weight about 80,000
Polyacrylate:	A polyacrylate homopolymer with an average molecular weight of 8,000 sold under the tradename PA30 by BASF GmbH
Protease:	Proteolytic enzyme sold under the trade name Savinase by Novo Industries A/S
Amylase:	Amylolytic enzyme sold under the trade name Termamyl by Novo Industries A/S
Silicate:	Sodium silicate (2.0 ratio)
Carbonate:	Sodium carbonate

PB4:	Sodium perborate tetrahydrate
PB1:	Sodium percarbonate monohydrate
PC:	Sodium percarbonate present in coated form, wherein the coating comprises a mixed salt of formula $Na_2SO_4.n.Na_2CO_3$ where n is 0.3.
PVNO:	Polyvinyl pyridine N-oxide polymer of molecular weight 10,000.
DAP:	Dioctanoyl acyl peroxide of formula $(CH_3(CH_2)_6CO_0)_2$, present as a urea clathrate.
TAED:	Tetraacetylethylenediamine
Paraffin:	Paraffin oil, sold under the tradename Winog 70 by Wintershall

Example 1

The following granular machine dishwashing detergent composition were prepared.

	A	B	C	D	E
Citrate	37.0	37.0	37.0	37.0	29.0
Silicate	25.7	25.7	25.7	25.7	25.7
PB1	-	-	-	-	1.9
PB4	8.0	8.0	-	8.0	8.7
TAED	4.1	4.1	-	4.1	4.4
DAP	-	0.5	0.5	-	0.5
PC	-	-	10.4	-	-
PVNO	-	-	-	0.5	-
Protease	2.2	2.2	2.2	2.2	2.2
Amylase	1.5	1.5	1.5	1.5	1.5
Benzotriazole	-	-	-	-	0.3
Paraffin	0.5	0.5	0.5	0.5	0.5
Nonionic	1.5	1.5	1.5	1.5	1.5
HEDP	-	-	-	-	0.5
Polyacrylate	-	3.7	3.7	-	3.7
MA/AA	3.7	3.7	3.7	3.7	-
Misc/moisture to balance					
pH (1% solution)	10.7	10.7	10.7	10.7	10.7

Compositions B, C and E contain DAP in accord with the invention. Compositions A and D are prior art compositions.

Test method 1

The ability of Compositions A, B and D to prevent the transfer of bleachable food soils to a plastic substrate was assessed using the following representative test method.

1. A representative bleachable food soil containing cartenoid type soils was prepared by liquidising equal quantities by weight of baked beans in tomato sauce, pasta sauce ("Ragu" tradename), Tandoori marinade and blackcurrant jam.

2. Plastic test samples were washed in a Sotax machine (which simulates dishwasher conditions) set at 200 rpm speed using an aqueous wash solution containing 4g per litre of water of one of the test detergent compositions and 9g per litre of water of the representative bleachable food soil. The water was of 8% German hardness (Ca:Mg = 3:1, equivalent to 1.44 mmol Ca^{2+}/litre). The wash temperature was 50°C at the start of the cycle, falling to 40°C at the end of the cycle, with each wash cycle lasting 30 minutes.

3. Each of the plastic test samples was submitted to 3 consecutive wash cycles. The plastic test samples were then removed, dried and visually graded for staining using a 4 point Scheffé scale.

Test method 1 - results

The presence of bleachable soil staining apparent on the plastic samples obtained using Compositions B and D as the detergent was compared to that obtained for the reference (Composition A).

	B/A	D/A
Degree of staining	+3.5	+1.0

(positive number indicates less staining for X versus Y).

The degree of staining obtained for composition B in accord with the invention was less that obtained for the reference composition A or for the comparative composition D which contained the polymeric dye transfer inhibiting agent PVNO.

Test method 2

The bleachable food soil stain removal from soiled plasticware capability of composition B was compared to that of reference Composition A using a modified version of test method 1. The plastic test samples were prestained by being soaked in the representative bleachable food soil for two days. These samples were then washed using an indentical protocol to that of test method 1, other than that no additional soil was added to the wash solution. The samples were graded visually for stain removal after the 3rd successive wash cycle.

Test method 2 - results

	B/A
Stain removal	+3.0

The bleachable food stain removal of composition B is enhanced versus that of reference Composition A in accord with the invention.

Example 2

The following tablet formulations in accord with the invention were prepared by a tablet compaction process.

	F	G	H
Citrate	23.7	23.7	23.7
Silicate	23.8	23.8	23.8
Carbonate	-	14.0	-
PB1	1.4	1.4	5.6
PB4	6.2	6.2	6.2
TAED	3.4	3.4	3.4
DAP	0.5	0.5	0.5
Protease	1.5	1.5	1.5
Amylase	1.1	1.1	1.1
Paraffin	0.4	0.4	0.4
Nonionic	0.2	0.2	0.2
Benzotriazole	0.3	0.3	0.3
HEDP	0.6	0.6	0.6
Polyacrylate	2.9	2.9	2.9
DETPMP	0.4	0.4	0.4
Na_2SO_4	33.1	19.1	28.9
Moisture/misc to balance			

Example 3

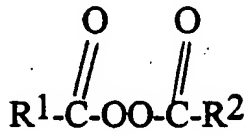
The DAP component of each of Compositions B, C and E of Example 1 and Compositions F, G and H of Example 2 was replaced by dibenzoyl peroxide at identical levels of incorporation in the compositions.

CLAIMS

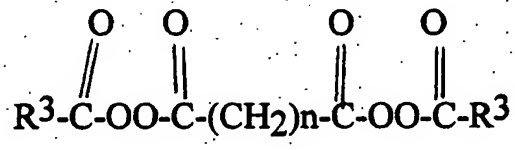
1. The use of a bleaching species to inhibit the transfer of a bleachable food soil from an aqueous wash solution to a substrate in a dishwashing method wherein said bleaching species is selected from diacyl and tetraacyl peroxide bleaching species and mixtures thereof.

2. The use according to Claim 1 wherein said method is a machine dishwashing method.

3. The use according to either of Claims 1 or 2 wherein said diacyl peroxide bleaching species is selected from diacyl peroxides of the general formula:



in which R^1 represents an aromatic group or a C_6-C_{18} alkyl group containing a linear chain of at least 5 carbon atoms and optionally containing one or more substituents (e.g. $-N^+(CH_3)_3$,-COOH or -CN) and/or one or more interrupting moieties (e.g. -CONH- or -CH=CH-) interpolated between adjacent carbon atoms of the alkyl radical, and R^2 represents an aliphatic or aromatic group compatible with a peroxide moiety, such that R^1 and R^2 together contain a total of 8 to 30 carbon atoms, and wherein said tetraacyl peroxide bleaching species is selected from tetraacyl peroxides of the general formula:



in which R^3 represents an aromatic group or a C_1-C_9 alkyl group, and n represents an integer from 2 to 12 inclusive.

4. The use according to Claim 3 wherein said R^1 and R^2 are phenyl groups.

5. The use according to any of Claims 1-4 wherein said bleachable food soil is a carotenoid soil.

6. The use according to any of Claims 1-5 wherein said substrate comprises plastic material.

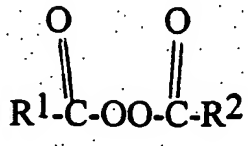
7. The use according to Claims 1-6 wherein said aqueous wash solution comprises said bleaching species at a level of from 1 to 100 ppm by weight of the wash solution.

8. The use according to Claim 7 wherein said aqueous wash solution comprises said bleaching species at a level of from 5 to 50 ppm by weight of the wash solution.

9. The use of a bleaching species to enhance the removal of bleachable food soils from a plastic substrate in a dishwashing method employing an aqueous wash solution wherein said bleaching species is selected from diacyl and tetraacyl peroxide bleaching species and mixtures thereof

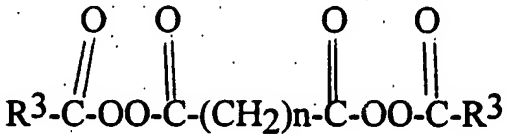
10. The use according to Claim 9 wherein said method is a machine dishwashing method.

11. The use according to either of Claims 9 or 10 wherein said diacyl peroxide bleaching species is selected from diacyl peroxides of the general formula:



in which R^1 represents an aromatic group or a C_6-C_{18} alkyl group containing a linear chain of at least 5 carbon atoms and optionally containing one or more substituents (e.g. $-N^+(CH_3)_3$, -COOH or -

CN) and/or one or more interrupting moieties (e.g. -CONH- or -CH=CH-) interpolated between adjacent carbon atoms of the alkyl radical, and R^2 represents an aliphatic or aromatic group compatible with a peroxide moiety, such that R^1 and R^2 together contain a total of 8 to 30 carbon atoms, and wherein said tetraacyl peroxide bleaching species is selected from tetraacyl peroxides of the general formula:



in which R^3 represents an aromatic group or a C_1-C_9 alkyl group, and n represents an integer from 2 to 12 inclusive.

12. The use according to Claim 11 wherein said R^1 and R^2 are phenyl groups.

13. The use according to any of Claims 9-12 wherein said bleachable food soil is a carotenoid soil.

14. The use according to Claims 9-13 wherein said aqueous wash solution comprises said bleaching species at a level of from 1 to 100 ppm by weight of the wash solution.

15. The use according to Claim 14 wherein said aqueous wash solution comprises said bleaching species at a level of from 5 to 50 ppm by weight of the wash solution.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/00571

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :A47L 15/02; C11D 3/20, 3/39, 3/395, 7/26, 7/38, 7/54
US CL :134/25.2; 252/95 102, 186.46
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 134/25.2; 252/95 102, 186.46

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,544,473 [KITCHEN] 01 December 1970 See Col. 1, lines 30-60.	1-4 & 9-12
Y	US, A, 4,134,850 [McCRUDDEN] 16 January 1979 See Col. 2, line 55 through Col. 3, line 25.	1-4 & 9-12
Y	US, A, 4,225,451 [McCRUDDEN] 30 September 1980 See Col. 4, lines 15-37.	1-4 & 9-12
A	US, A, 4,464,281 [RAPISARDA] 07 August 1984 See Col. 7, lines 55-59.	1-4 & 9-12
Y	US, A, 5,230,822 [KAMEL] 27 July 1993 See Col. 6, lines 8-9 and Col. 15, lines 11-18.	1-4 & 9-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
26 APRIL 1995

Date of mailing of the international search report
30 MAY 1995

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Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/00571

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 5-8 and 13-15
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.